

Final Report  
Cooperative Agreement NCC 2-264  
Differences in Interfacial Bond Strengths  
of Graphite Fiber-Epoxy Resin Composites

Principal Investigator: Howard L. Needles  
Division of Textiles & Clothing  
University of California  
Davis, CA 95616

Prepared for: NASA-Ames

Moffett Field, CA 94035

{NASA-CR-176912} DIFFERENCES IN INTERFACIAL  
BOND STRENGTHS OF GRAPHITE FIBER-EPOXY RESIN  
COMPOSITES Final Report (California Univ.)  
26 p

N86-29905

CSCL 11D

Unclas

G3/24 43284

## Introduction

The role of the fiber-resin interface in determining the overall mechanical properties of composites is poorly understood (1-3). A good interfacial adhesive bond is required to achieve maximum stress transfer to the fibers in composites, but at the same time some form of energy absorbing interfacial interaction is needed to achieve high fracture toughening (3,4). The incompatibility of these two processes make it important to understand the nature and basic factors involved at the fiber-resin interface as stress is applied.

The mechanical properties including interlaminar shear values for graphite fiber-resin composites are low compared to glass and boron-resin composites. These differences have been attributed to poor fiber-matrix adhesion (1,5). Graphite fibers are commonly subjected to post-treatments including application of organic sizing in order to improve their compatibility with the resin matrix and to protect the fiber tow from damage during processing and lay-up (5).

In such processes, sized graphite fiber tow is impregnated with epoxy resin and then layed-up into the appropriate configuration. Following an extended ambient temperature cure, the graphite-resin composite structure is cured at elevated temperature using a programmed temperature sequence to cure and then cool the product.

In this study, the effect of epoxy-size and degree of cure on the interfacial bonding of an epoxy-amine-graphite fiber composite system is examined.

## Experimental Materials

The graphite fiber tows used in the study were from a commercial source and had a nominal tensile strength of  $3.79 \times 10^6$  KPa (550,000 psi) and a modulus of  $2.4 \times 10^8$  KPa ( $3.5 \times 10^7$  psi). Both unsized and epoxy-sized graphite fiber tows were used. An extracted graphite fiber tow was prepared by extracting the epoxy-sized tow soxhlet extractor with methylene dichloride for 8 hrs. at 40-45°C.

An aromatic epoxy-amine resin system was used consisting of a mixture of the diglycidyl ethers of Bisphenol A and 1,4-butanediol and a mixture of aromatic diamines (6). The advancing and receding contact angles of sized and unsized fiber in epoxy-amine resin were measured by a previously described technique (7).

#### Composite Formation and Preparation for Testing

The mold used has been described previously (8) and is based on a system by Broutman and McGarry (9) for preparing composite samples for measurement of interfacial bond strengths. The mold was thoroughly cleaned, dried, and sprayed with a Teflon mold lubricant (Tiolon X 20). Graphite fiber tow was coated on both sides with epoxy-amine resin by means of a glass rod applying pressure to the fibers to ensure maximum penetration of epoxy-amine resin into the fiber bundle. The fibers were allowed to stand one hour and then mounted in the mold. The mold was closed and then filled with epoxy-amine resin. The mold was allowed to stand at 21°C for 2 or 3 days or for a longer period if the sample was only to be cured at room temperature. Samples cured for 2 or 3 days were then heated and cured at elevated temperature according to the following temperature program. The temperature of the samples was raised from 25°C to 165°C at a rate of 30°C per hr. The temperature then was held at 165°C for 3 or 17 hrs, followed by cooling at a rate of 20°C per hr. until room temperature was reached. The samples of fiber tows imbedded in epoxy-amine resin were removed from the mold and excess graphite fiber removed from the surface and the surface smoothed by sanding. The samples were cut into 1/2" blocks using a band saw for non-heat-cured samples and a circular saw for heat-cured samples. Cured resin samples without imbedded graphite fiber were prepared also.

### Compression Tensile Testing

The samples were tested on a Tinius-Olsen tensile testing machine at a compression rate of 0.635 mm/min. (0.025"/min). Composite samples broke catastrophically and were collected for scanning electron microscopy (SEM).

### Composite Cross-sectioning

Cross-sections of graphite-epoxy-amine composite samples were prepared as follows: Samples were cooled in liquid nitrogen and fractured by a sharp blow perpendicular to the fiber axis to provide a cross-section sample. Cross sections of samples were also cut by use of a razor blade or glass microtome blade. The razor and microtome cut samples were coated with two coats of silver and scanning electron micrographs taken. Then, the samples were cured as follows: The temperature of the samples was raised from 25°C to 177°C at a rate of 16.7°C (30°F per hour). The samples were maintained at 177°C for 3 hrs and then cooled at 16.7°C (30°F) per hour to 25°C.

### Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the graphite fibers and the interfaces of broken graphite-epoxy-amine composites coated with two coats of silver were taken on a ISI DS-130 using lab 6 filament operating at 10 Kv and a magnification of 300 to 3,500X.

### Results and Discussion

The nature of interfacial bonding and adhesion in the graphite fiber tow-epoxy-amine resin system was studied with particular emphasis on the effect of epoxy-compatible size and degree of cure on the nature of interfacial bonding. Contact angle measurements for graphite fibers and epoxy-amine resin, compressive strengths at failure for epoxy-amine resin alone and for graphite fiber-epoxy-amine composites, and scanning electron microscopy of graphite fiber and composite samples undergoing compressive failure, freezing and fracture, or



cutting were used to characterize the nature of adhesion and failure at the fiber-resin interface.

Wetting of the graphite fiber surface by epoxy-amine resin is critical in order to achieve a high degree of adhesive bonding at the fiber-resin interface (5,6-8,10). In general, carbon fibers have similar wettabilities to epoxy resin systems. The advancing and receding contact angles for sized and unsized graphite fibers wet with freshly prepared epoxy-amine resin were measured (Table I). Both the sized and unsized graphite fibers were readily wet by the resin. Although the contact angles for sized graphite fiber were slightly less than that for unsized fiber, the differences were not statistically significant. Therefore, the sized surface was as readily wet by resin as the unsized surface.

The interfacial bond strengths of single graphite fibers suspended in high performance resins were measured previously (7,8,10). This test used a special curved-neck specimen similar to that used by Broutman and McGarry (9). On compression the adhesive bond between resin and filament fails due to radial tensile stress created at the interface by the differing Poisson's ratio between the filament and the resin. However, the compression strains placed on the high modulus single graphite fiber in the fiber-epoxy matrix cause fiber fracture before debonding occurs (10), therefore the interfacial bond strengths observed represent only minimum nominal values. In our study we wished to consider the interfacial bond strengths of graphite fiber tows imbedded in epoxy-amine resin. We expected that individual fiber breakage of a lower modulus fiber in a strong matrix resin would be eliminated as a factor in determining interfacial bond strengths. However, it was found that the compressive strengths at failure were similar for all resin only and fiber-resin samples having the same cure, although the nature of failure differed between resin only and fiber resin composite samples (Table II). While the fiber-resin samples underwent catastrophic failure,

the resin only samples underwent compressive crazing and thickening and bulging of the narrowest portion of the cross-section. Therefore, it is believed that the compressive stress values represent the compressive strength of the resin in the presence and absence of tow rather than the interfacial bond strengths. Although the interfacial bond strengths could not be measured by this method, the catastrophic failure of fiber-resin specimens permitted analysis of the failed interface by scanning electron microscopy.

The nature of unsized, sized, teflon-treated sized, and extracted sized graphite fibers and of the failed or cross-sectioned interface of composites of these fibers with epoxy-amine resin were examined by scanning electron microscopy (Figures 1-4). As expected, the unsized fibers were smooth and without surface characteristics (Figure 1a). On compressive failure, the unsized fibers in the cured composite (17 hrs.) broke away freely from the cured resin (Figure 1b), and there was little evidence of adhesion of the resin to the fiber surface. At higher magnification, spaces between the fiber surfaces and the epoxy matrix was observed (Figure 1c). This space between the fiber surfaces and the resin matrix may be due to shrinkage in the epoxy during curing at elevated temperature.

The presence of epoxy-compatible size could readily be seen on the surface of the sized fiber tow (Figure 2a). Examination of the cut tow showed that the size was confined primarily to the surface, and did not penetrate far into the fiber bundle (Figure 2b). Compressive fracture of the low temperature cured, sized fiber-resin matrix demonstrated some adhesion of resin and/or size to the surface of graphite fibers (Figures 2c,2d). On high temperature curing and compressive fracture of this system, there was evidence for good penetration of epoxy-amine resin into the interior of the tow. Significant shrinkage of resin away from individual carbon fibers was evident at shorter and extended high temperature cure times (Figures 2e,2f,2g,2h,2i).

Samples of the high temperature cured, sized fiber-resin composites were cooled in liquid nitrogen and fractured. Scanning electron microscopy of the fiber-resin matrix at the point of fracture and near the edge of the fiber bundle near where the size should be present revealed no evidence of adhesion between the fiber and resin matrix at either curing time (Figures 2j,2k,2l,2m). Also, any remaining size could not be detected within the resin matrix.

The sized graphite fibers were also sprayed with Teflon and then embedded in epoxy-amine resin and high temperature cured. The fractured composite showed a wide distribution of Teflon throughout the resin matrix suggesting that considerable migration within the resin occurs during the cure at elevated temperature (Figures 2n,2o). Nevertheless, Teflon particles could be seen at the fiber surface and no evidence of adhesion on the fiber surface was observed.

Solvent extraction readily removed the size from the surface of the fibers (Figure 3a). Fracture of the high temperature cured, extracted fiber-resin composites shows penetration of epoxy throughout the fiber bundle, and little evidence for adhesion of resin to the fibers was found (Figures 3b,3c,3d). Limited adhesion occurred between fiber and resin, however (Figure 3d).

Attempts were made to cross-section the fiber-polymer composite cured at room temperature using either a razor blade or a glass microtome blade. The cross-sectioned samples were then coated with silver and prepared for scanning electron microscopy. After scanning electron micrographs of the samples were taken (Figure 4a,4c), samples were subjected to a high temperature cure procedure holding the cure at 177°C for 3 hours. Then a second set of scanning electron micrographs were taken (Figure 4b,4d). No significant differences in the scanning electron micrographs could be seen.

In summary, the size has little effect on adhesion of the epoxy-amine resin to the graphite fiber surface. At room temperature, extensive adhesion of resin

and/or size to the fiber surface was observed. On curing at high temperatures, shrinkage of the epoxy-amine resin occurred and little adhesion was found in the fiber-resin matrix. The adhesion observed appears irregularly along the fiber surface.

### Conclusion

For the graphite fiber-epoxy-amine composite system studied, the following conclusions can be made with regard to the nature of the fiber-resin interface: The resin readily wets and penetrates the graphite fiber bundle even in the presence of size. The interfacial bond strength of the fiber tow-resin interface cannot be measured by adapting the single fiber method. On curing at room temperature, extensive adhesion of resin and/or size to the fiber surface was observed. At high temperature cures, little adhesion of resin to the fiber surface was observed, and the presence of the size did not significantly alter the amount of adhesion. Shrinkage of the resin away from the graphite fibers was observed and presumably accounted for the reduction in fiber adhesion due to high temperature curing. The points of adhesion remaining occurred randomly along the fiber surface.

## References

1. D. A. Scola and C. S. Brooks, J. Adhesion, 2, 213 (1970).
2. J. C. Goan and S. P. Prosen, Interfaces in Composites, ASTM STP 452, p. 3 (1969).
3. L. J. Broutman, Interfaces in Composites, ASTM STP 452, p. 27 (1969).
4. B. Harris, P. W. R. Beaumont and E. M. deFerran, J. Materials Sci., 6, 238 (1971).
5. G. Lubin, Ed., "Handbook of Composites", Van Nostrand Reinhold Co., N.Y., 1982.
6. T. T. Chiao, E. S. Jessop and H. A. Newey, SAMPE Quart., 6(1), 28 (1974).
7. D. S. Varma, H. L. Needles, D. A. Kourtides and R. H. Fish, Org. Coatings and Appl. Polym. Sci. Proc., 46, 105 (1981).
8. D. S. Varma, H. L. Needles, D. A. Kourtides and R. H. Fish, Polym. Composites, 4, 98 (1983).
9. L. J. Broutman and F. J. McGarry, Modern Plastics, p. 161 (Sept. 1962).
10. H. M. Hawthorne and E. Teghtsoonian, J. Adhesion, 6, 85 (1974).

Table I

The Effect of Size on the Contact Angles of Carbon Fibers Wetted  
with Epoxy-amine Resin

Graphite Fiber <u>Type</u>	<u>Contact Angle ( ° )</u>	
	<u>Advancing</u>	<u>Receding</u>
Unsize	15.9 ± 3.2	17.3 ± 2.7
Sized	12.1 ± 2.9	11.5 ± 2.9

Table II  
Apparent Compressive Strengths of Epoxy-Amine Resin and Carbon Tows Imbedded  
in Epoxy-Amine Resin Matrix

<u>Sample<sup>*</sup></u>	<u>Cure</u>	<u>Apparent Compression Strength (psi)</u>
EA	RT (55 days)	16,625 ± 799
EA	HT (17 hrs.)	20,293 ± 3,158
U-EA	HT (17 hrs.)	21,812 ± 2,263
S-EA	RT (28 days)	12,788 ± 1,125
S-EA	RT (55 days)	16,375 ± 1,188
S-EA	HT (17 hrs.)	19,608 ± 1,332
S-EA	HT (3 hrs.)	21,695 ± 918
ST-EA	HT (17 hrs.)	20,253 ± 3,411
E-EA	HT (17 hrs.)	23,169 ± 3,674

---

<sup>\*</sup> EA - Epoxy-amine matrix only; U-EA - unsized graphite fiber-epoxy-amine matrix; S-EA - sized fiber-epoxy-amine matrix; ST-EA - sized fiber coated with Teflon-epoxy-amine matrix; E-EA - extracted sized fiber-epoxy-amine matrix.

<sup>\*\*</sup> RT - Room temperature cure at 21°C for 28 to 55 days; HT - Room temperature cure followed by high temperature cure for 3 to 17 hrs.

Figure 1. (a) - Unsized graphite fiber tow (1,160X); (b),(c) - High temperature cured (17 hrs.) unsized graphite-resin interface on fracture (468X), (3,470X).

Figure 2. (a),(b) - Sized graphite fiber (363X) (439X); (c),(d) - Room temperature cured sized fiber-resin interface on fracture (1,740X), (3,100X); (e),(f) - High temperature cured (3 hrs.) sized fiber-resin interface on compressive fracture (2,040X), (5,410X); (g),(h),(i) - High temperature cured (17 hrs.) sized fiber-resin interface on compressive fracture (392X), 2,630X), (2,940X); (j),(k) - High temperature cured (3 hrs.) sized fiber resin matrix on freeze fracture (1,410X), (2,820X); (l),(m) - High temperature cured (17 hrs.) sized fiber-resin matrix on freeze fracture (9,090X) (15,300X); (n),(o) - High temperature cured (17 hrs.) Teflon-sprayed sized fiber-resin interface on fracture (143X), (2,880X).

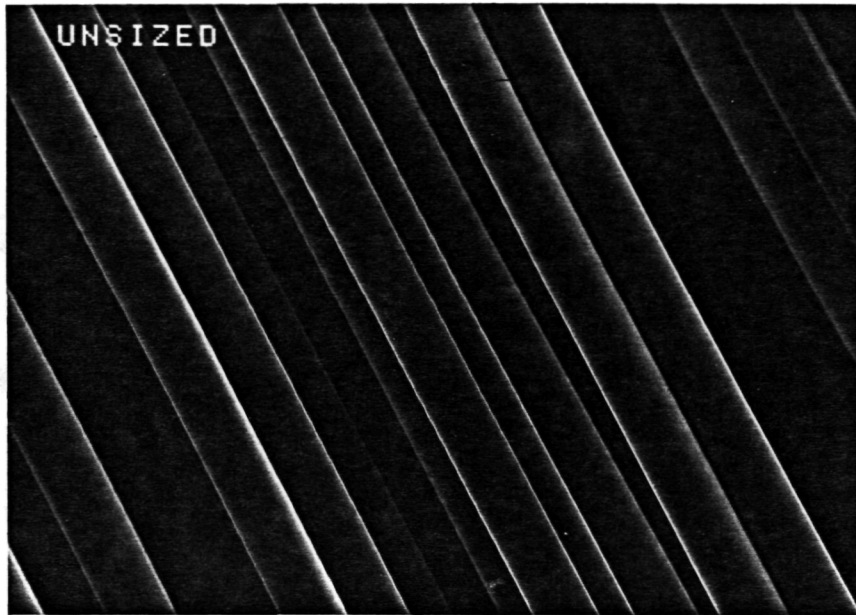
Figure 3. (a) - Solvent extracted sized fiber (2,040X); (b),(c),(d) - High temperature cured (17 hrs.) extracted sized fiber-resin interface on compressive fracture (1,040X), (3,100X), (2,860X).

Figure 4. (a),(b) - Room temperature cured sized fiber-resin interface with microtome and razor, respectively; (c),(d) - High temperature cured (3 hrs.) sized fiber-resin interface cut by microtome and razor, respectively.

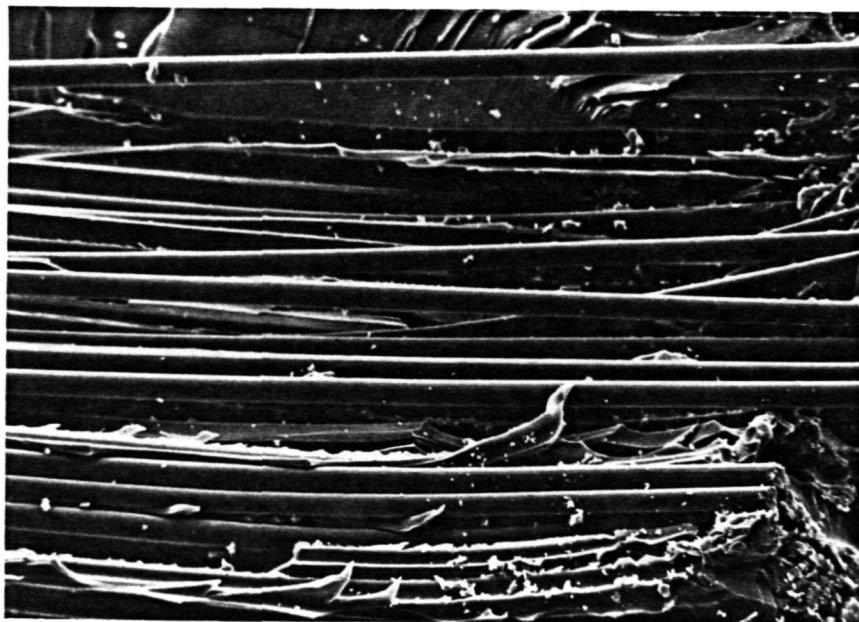


ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 1



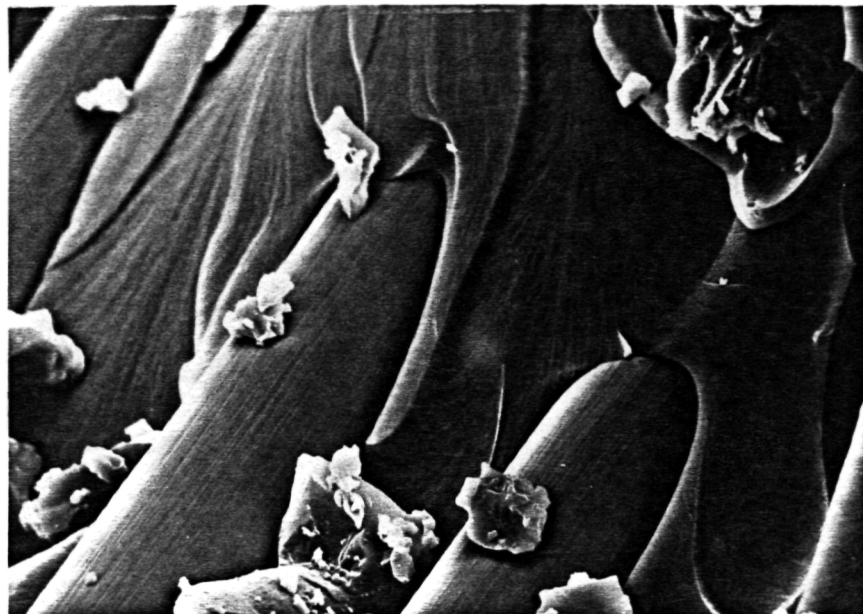
(a)



(b)

Figure 1

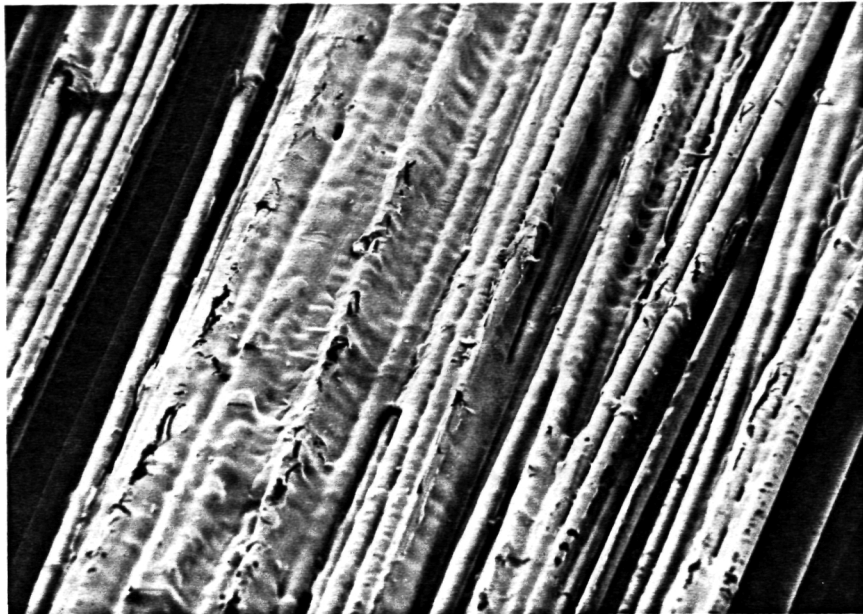
ORIGINAL PAGE IS  
OF POOR QUALITY



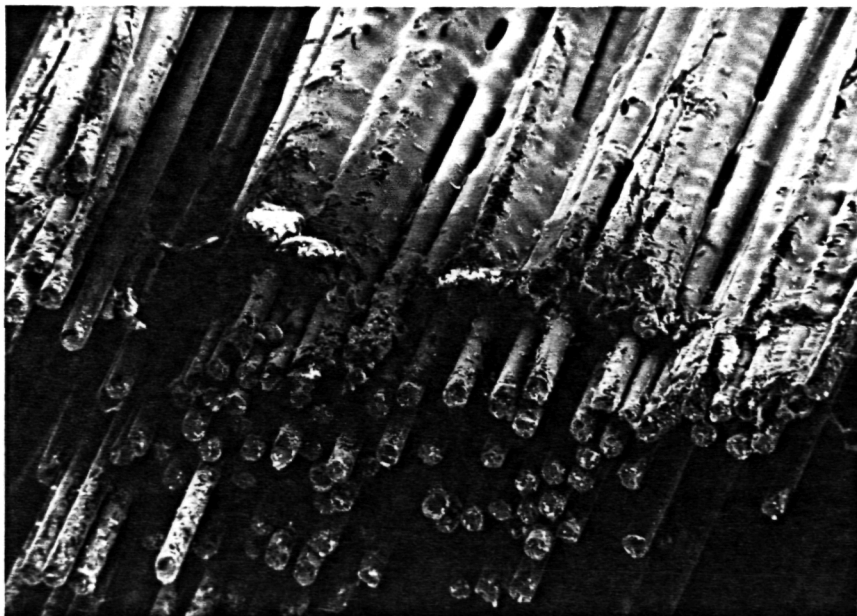
(c)

ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 2



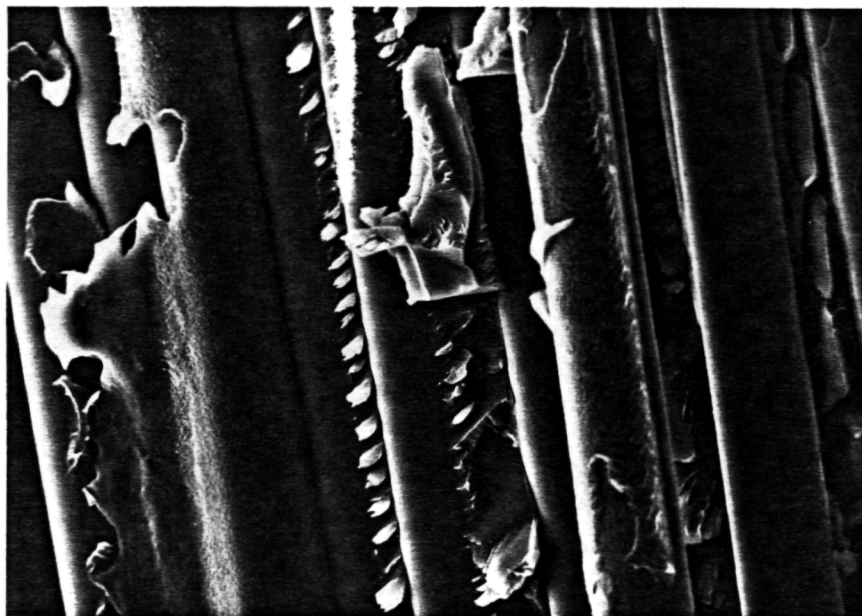
(a)



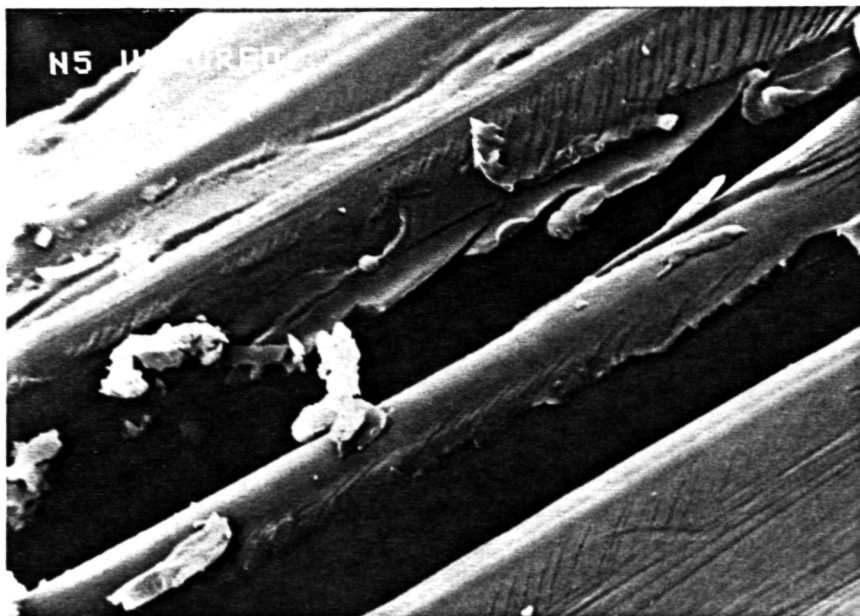
(b)

Figure 2

ORIGINAL PAGE IS  
OF POOR QUALITY



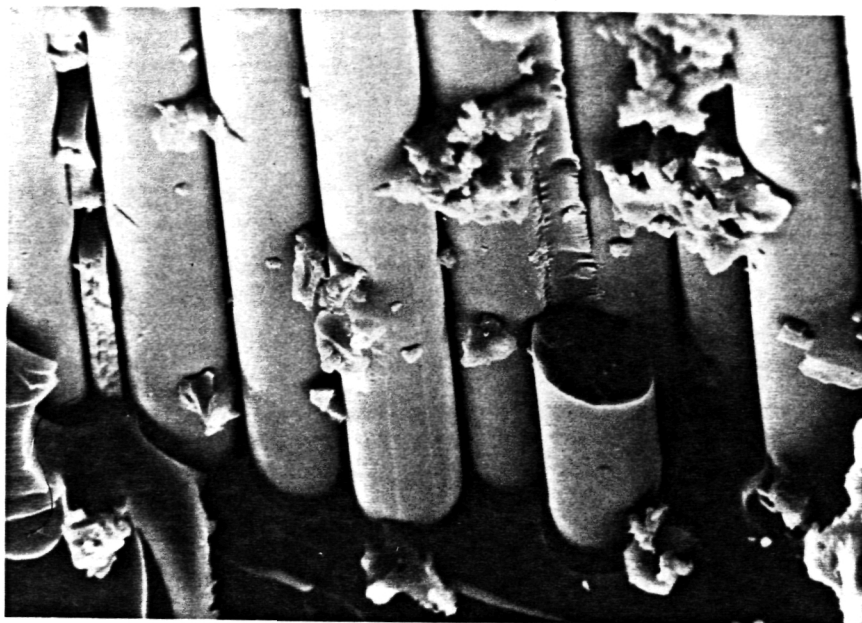
(c)



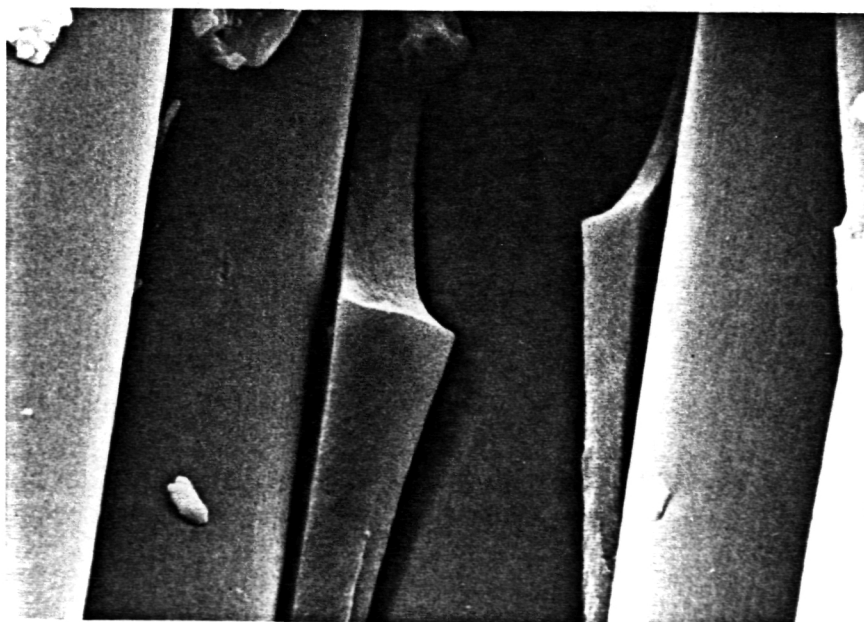
(d)

ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 2



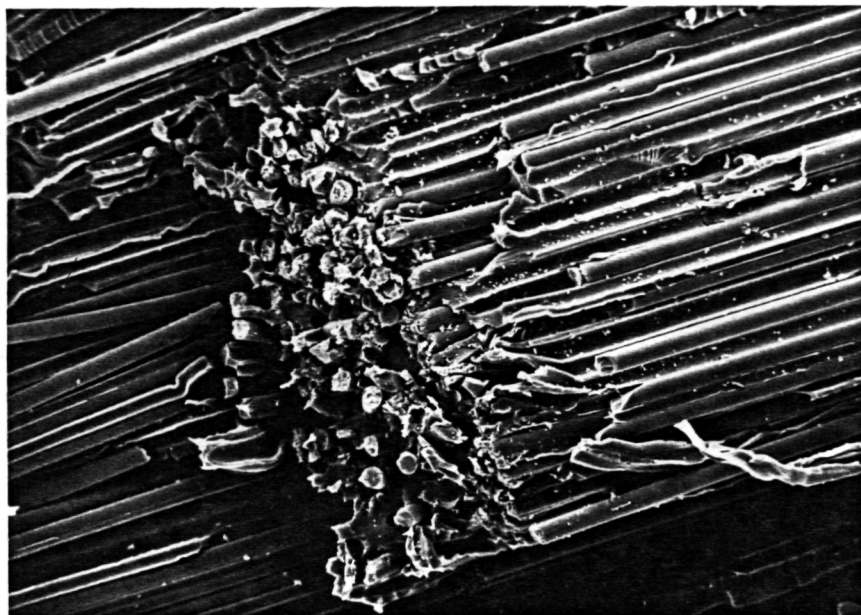
(e)



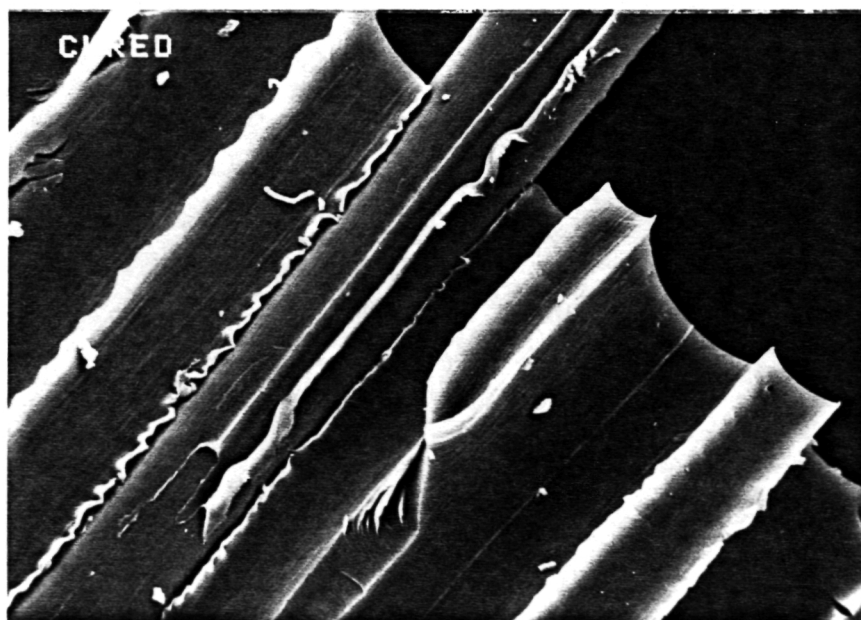
(f)

Figure 2

ORIGINAL PAGE IS  
OF POOR QUALITY



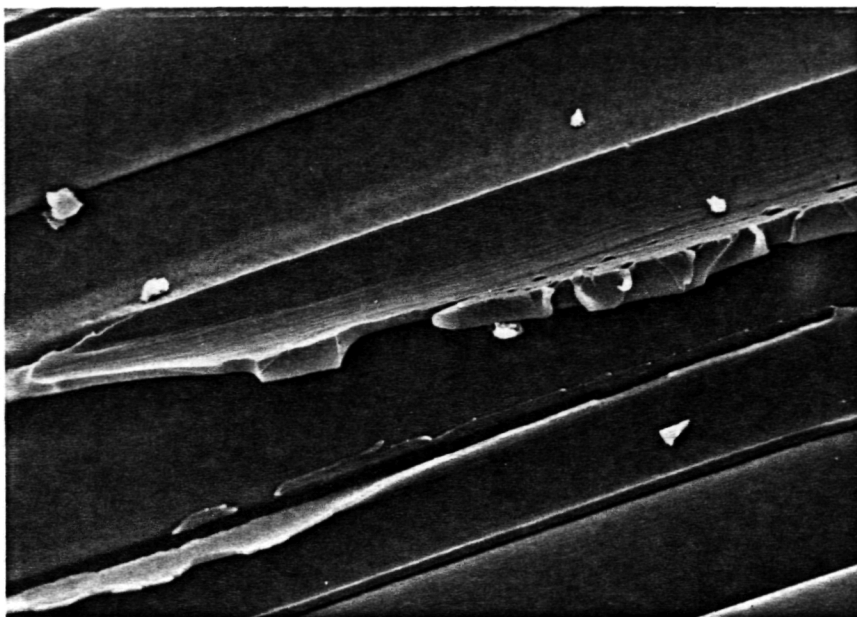
(g)



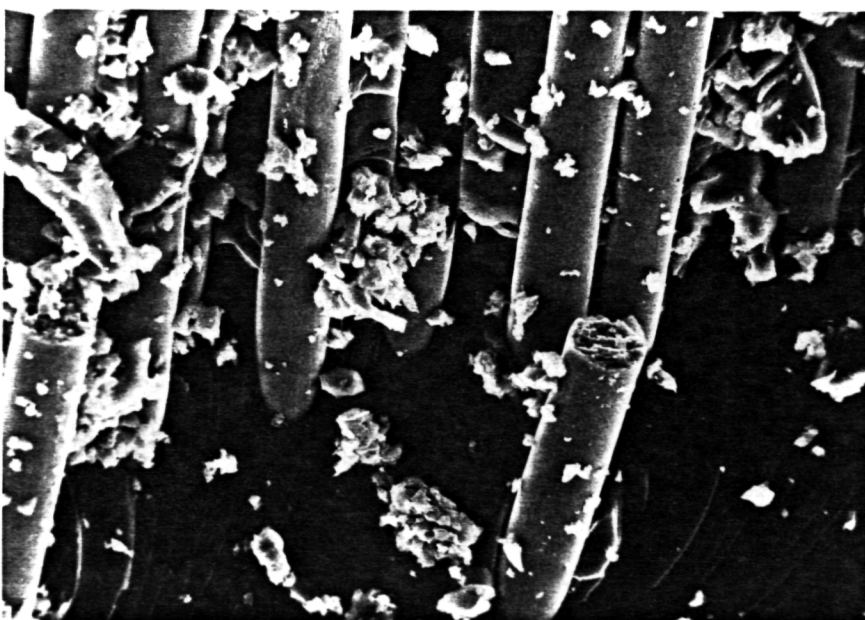
(h)



Figure 2



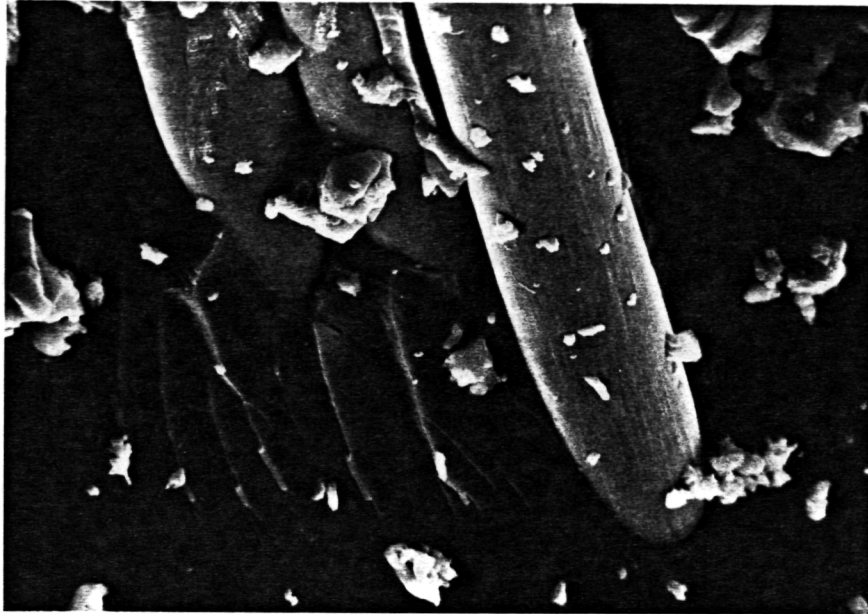
(i)



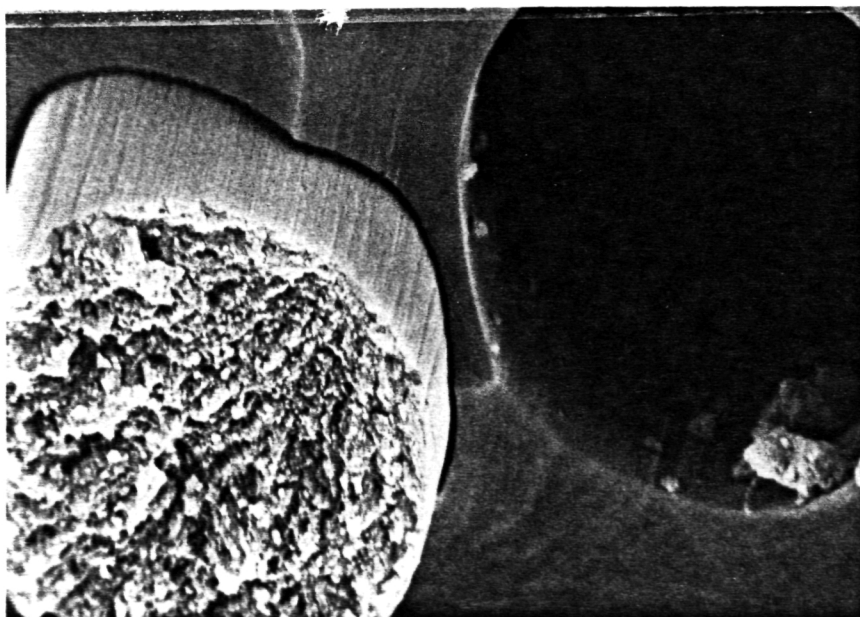
(j)

ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 2



(k)

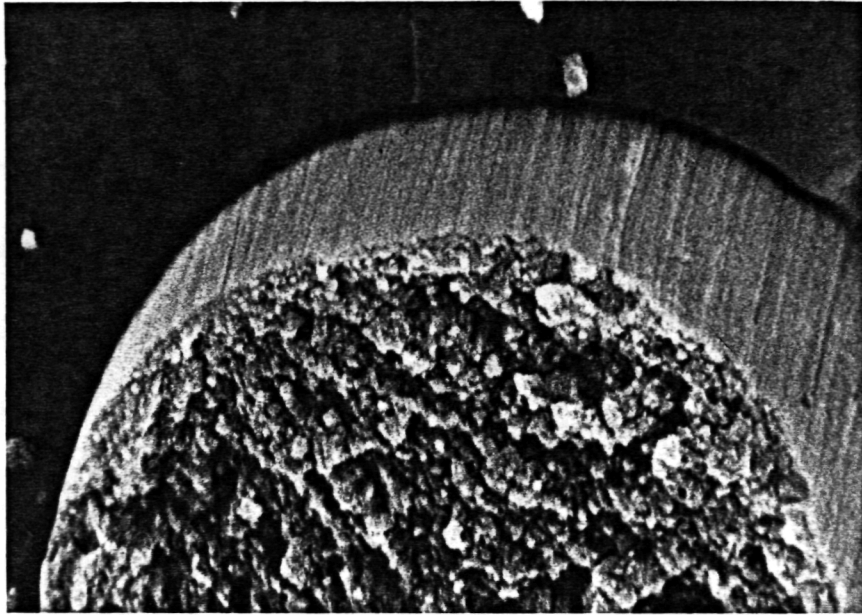


(l)

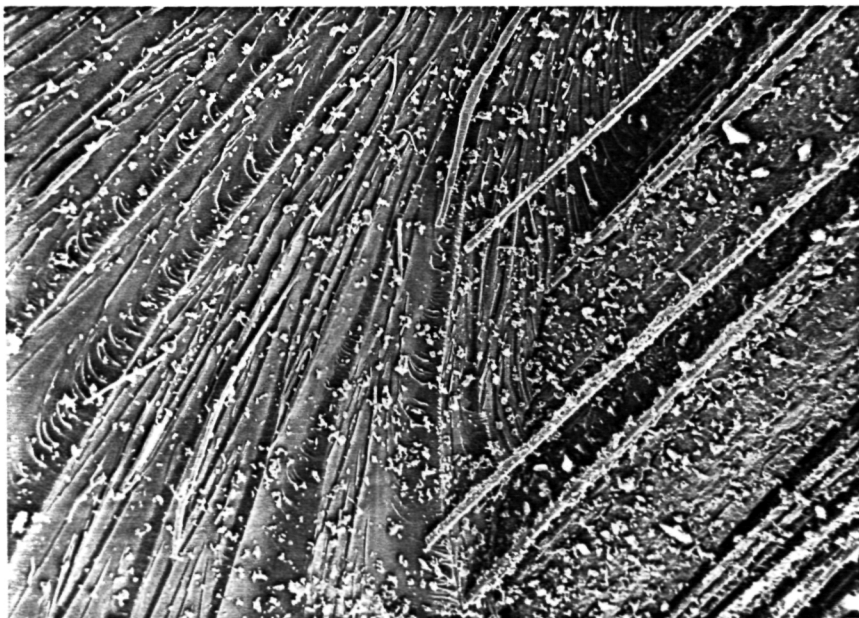


ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 2

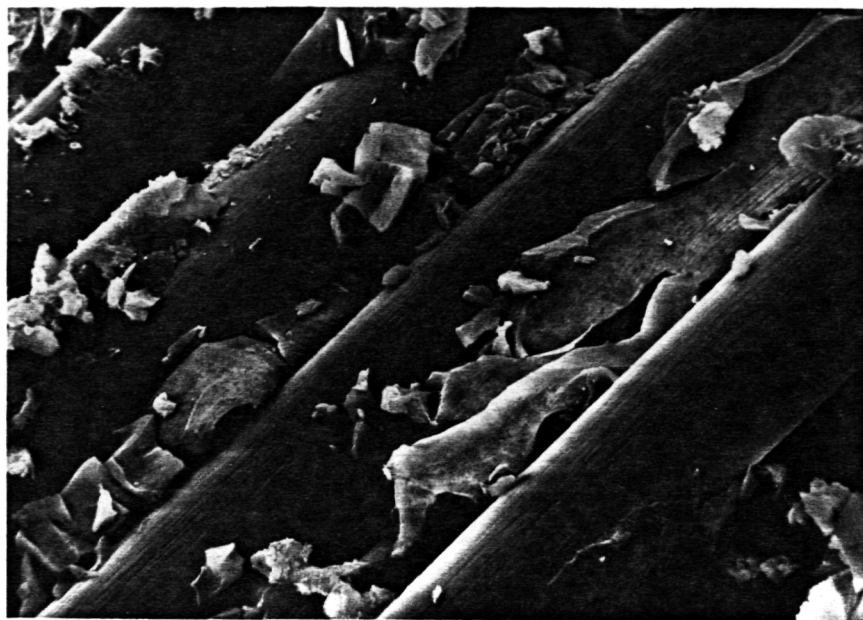


(m)



(n)

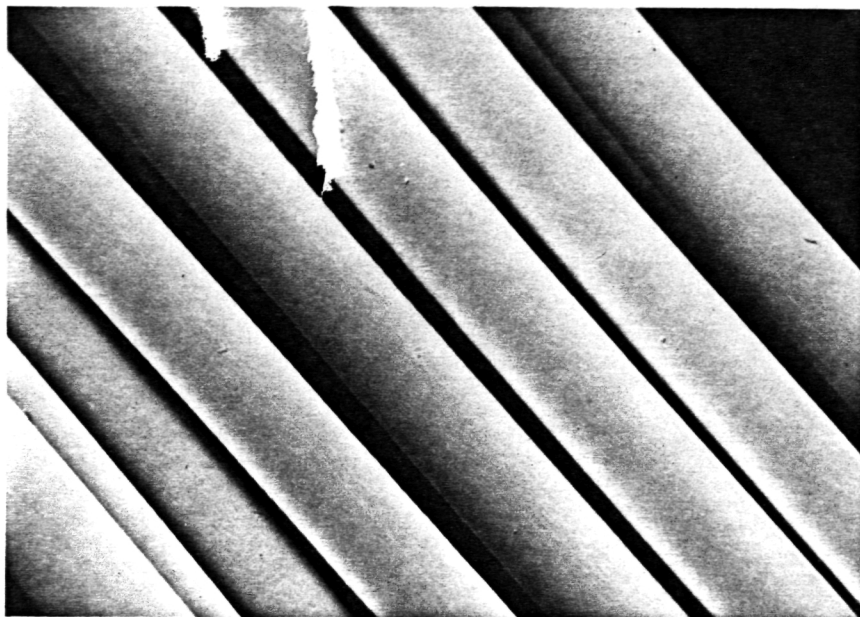
Figure 2



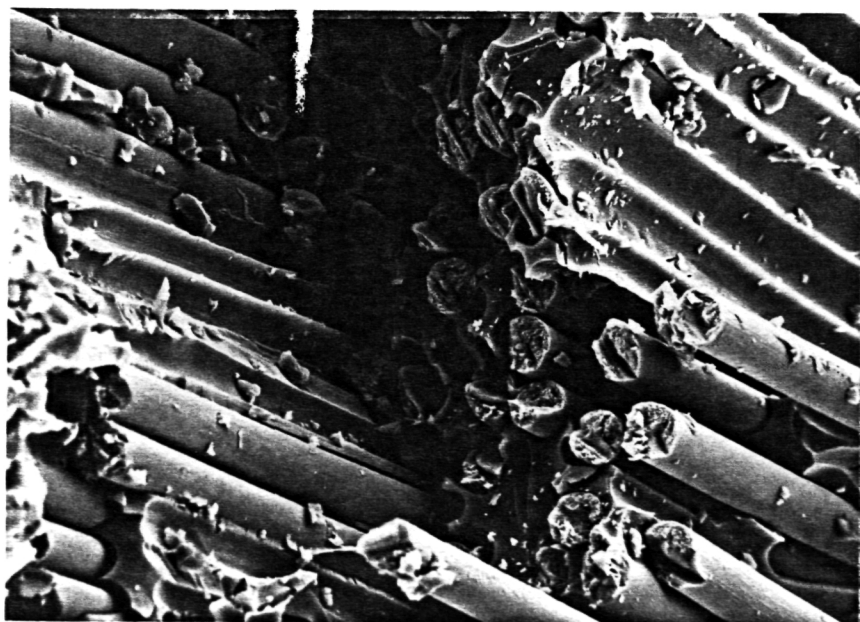
(o)

Figure 3

ORIGINAL PAGE IS  
OF POOR QUALITY

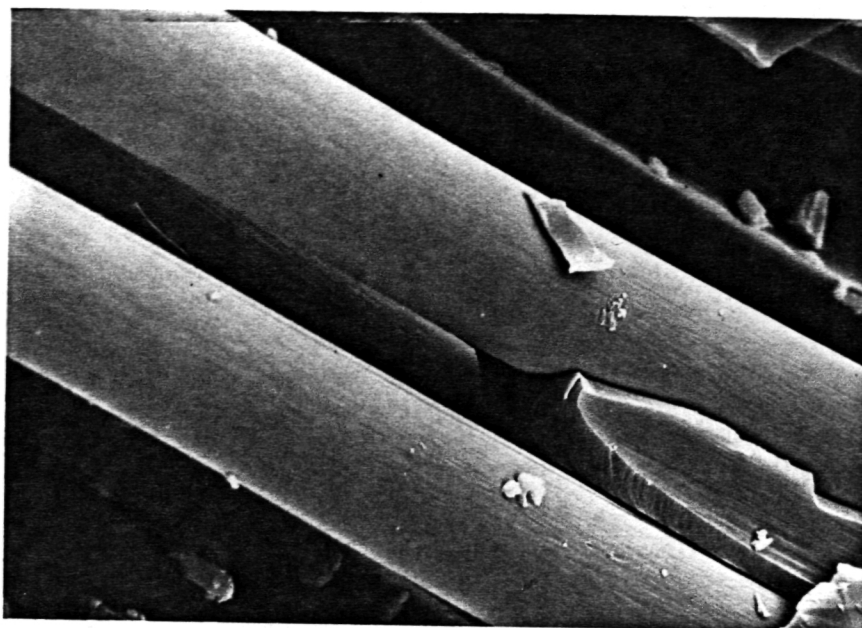


(a)

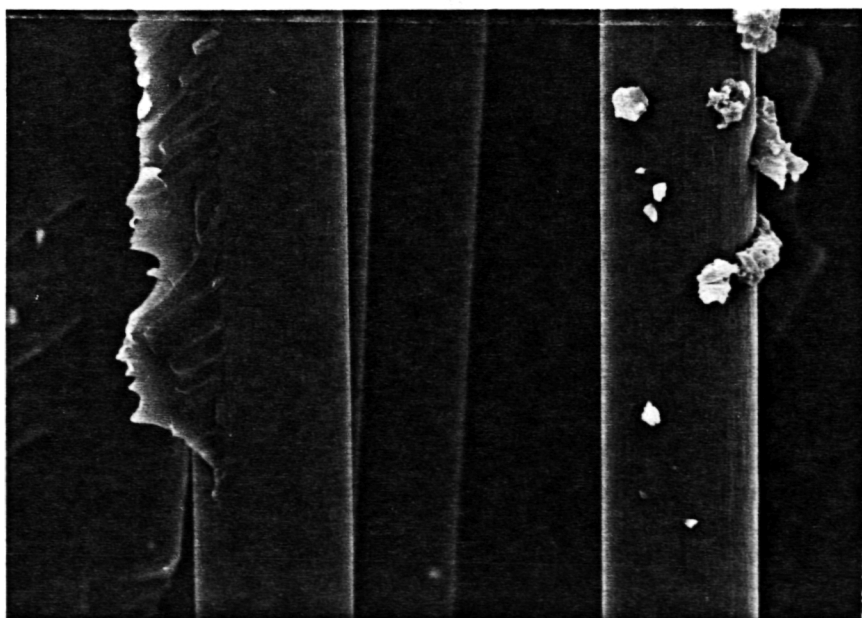


(b)

Figure 3



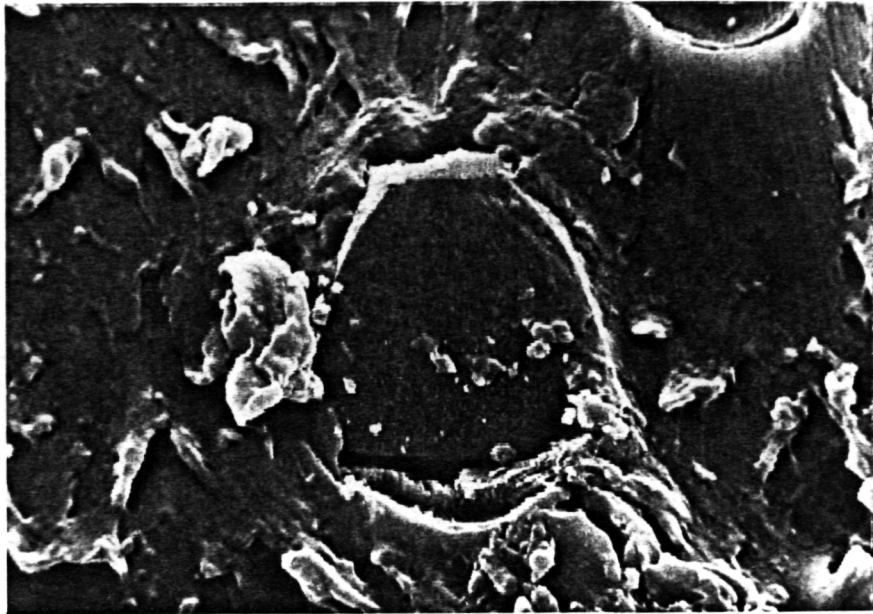
(c)



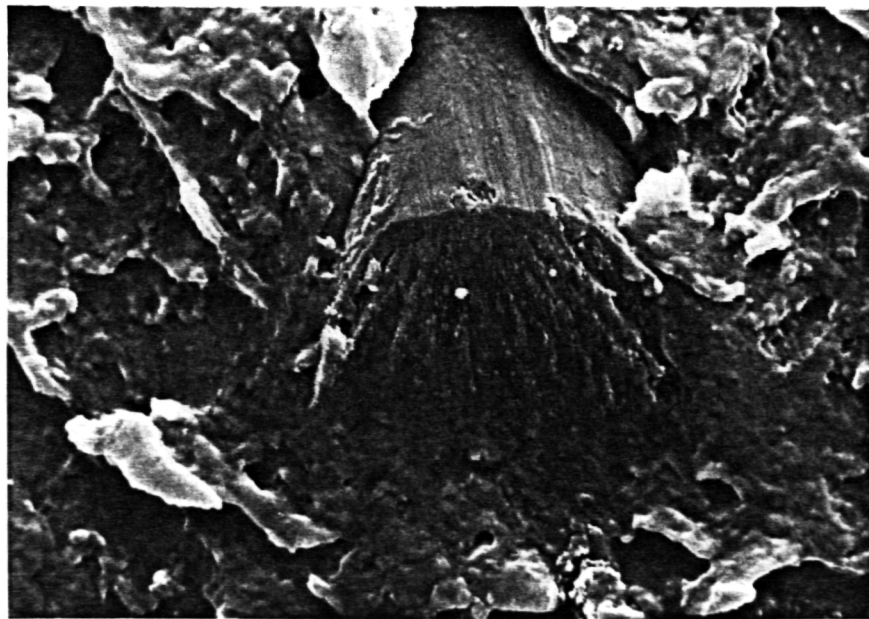
(d)

ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 4



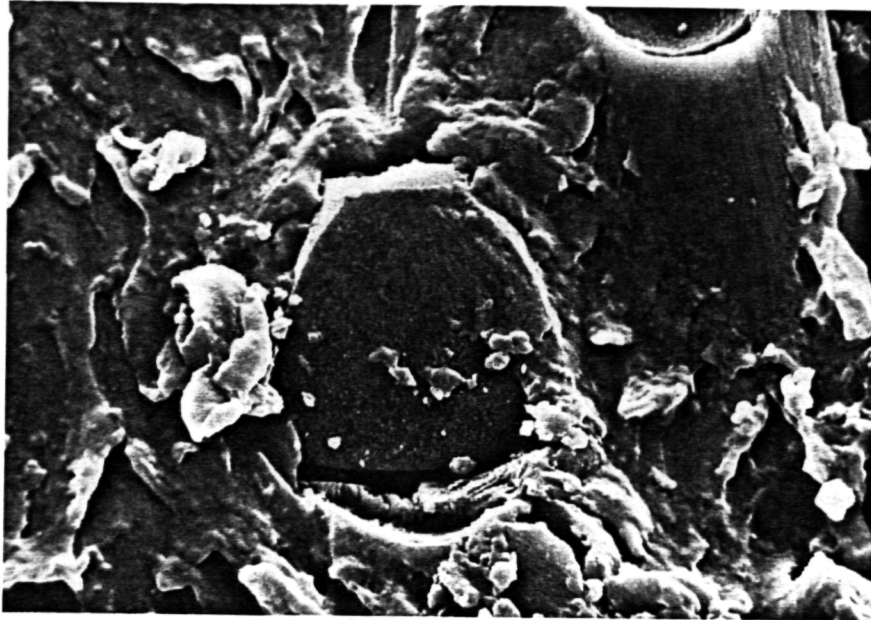
(a)



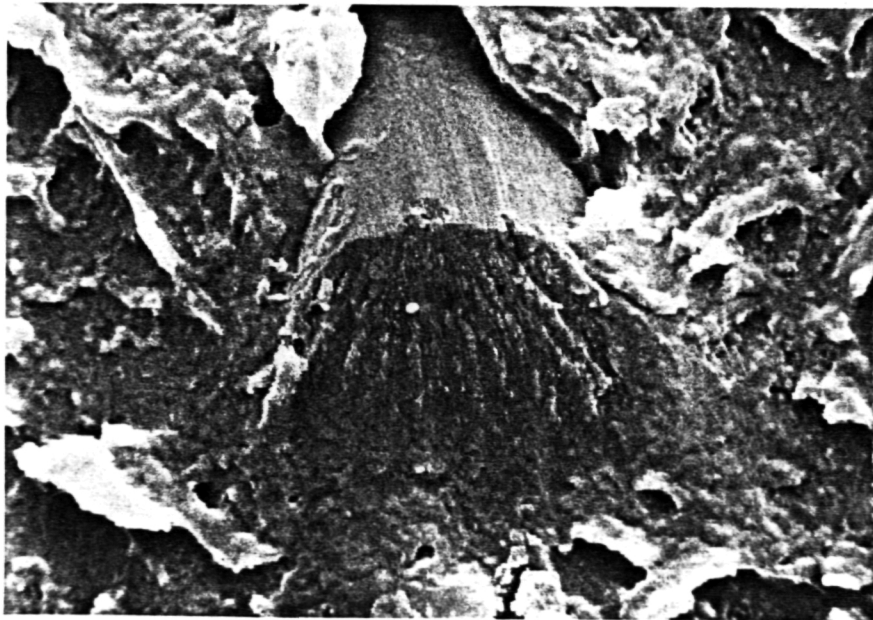
(b)

ORIGINAL PAGE IS  
OF POOR QUALITY

Figure 4



(c)



(d)